Polarisation of the Light Scattered by Mercury Vapour near the Resonance Periodicity.

By LORD RAYLEIGH, F.R.S.

(Received September 28, 1922.)

§ 1. Introduction.

When light belonging to the visual spectrum is scattered by air, as, for example, in the blue sky, there is no approximation to resonance between any period of vibration contained in the source and a free period of the scattering molecules or atoms. In such cases, there is an approach to complete polarisation of the scattered light, though a closer examination shows that the polarisation is in general incomplete. In argon, however, and probably in the other monatomic gases, there is a very near approach to completeness.*

In contrast with these cases is the scattering of light by mercury vapour in resonance with the source, when the latter belongs to the ultra-violet mercury line λ 2536, as emitted by a cooled mercury arc. This case was investigated by R. W. Wood.† He found that so long as the lamp ran under conditions favourable to producing an extremely narrow line without reversal, there was a copious emission of scattered light. I was anxious, 3 years ago, to trace the transition between this case and the ordinary scattering well away from the resonance periodicity. This was not fully achieved when my attention was turned to other matters, and shortly afterwards my laboratory at the Imperial College was dismantled. I have not since found an opportunity to resume, and it seems desirable to record the results, such as they are, without further delay.

§ 2. Qualitative Detection of Polarisation.

The mercury are used was contained in a long vertical silica tube. A tungsten rod anode passed in at the top through a rubber connection and a side tube made connection with an exhausted glass flask, to afford a reservoir of vacuum, if the expression may be allowed. The cathode was the top surface of a barometric column standing in the tube, and the arc was struck by raising the reservoir till the mercury came in contact with the anode. A brass jacket with a quartz window was provided to keep the arc cool by water circulation, and the transverse field of a small electro-magnet kept the arc

^{* &#}x27;Roy. Soc. Proc.,' A, vol. 98, p. 57 (1920).

^{† &#}x27;Phil. Mag.,' vol. 23, p. 689 (1912).

pressed against the front wall of the tube, so as to squeeze out the cooler layer of mercury vapour which otherwise intervenes.* The quartz tube was 8 mm. in diameter, and the current found to give the best result was about 10 ampères.

The light from this lamp was limited by a diaphragm about 1 cm. square, and made parallel by a quartz lens of short focus. The beam traversed a vessel exhausted of air and containing mercury vapour at the ordinary temperature. This vessel was made of square brass tubing, blackened inside, and had plane windows of silica glass, ground and polished. This material has a trace of double refraction,† but so very slight as not perceptibly to complicate the present experiments. The vessel was blackened internally, and the beam passed across the mouth of a cave or tunnel of some 10 cm. depth, which afforded a black background, as in previous experiments on scattering.

The first experiments were made with a view to detecting the existence of polarisation which Wood's early experiments had not revealed. It was thought that this might be attained if the light were filtered through a stratum of cold mercury vapour, in order to absorb the central constituent of the exciting spectrum line.

The polarising prisms used were a pair of quartz Wollaston prisms, made for me by Messrs. Hilger. For ultra-violet light it is necessary to avoid the use of Canada balsam, and the two halves of the prisms were put together in optical contact, like the echelon gratings made by the same firm. Only a very faint reflection could be seen from the interface. The two prisms were used in series, as the separation given by one alone was inconveniently small.

A camera with a simple quartz lens was mounted so that the axis of the latter was perpendicular to the primary beam traversing the vapour, and in front were the two Wollaston prisms set so as to separate the two polarised components in the up and down direction. In this way a photograph of the two components in the transverse direction could be taken, and it was found that the difference in intensity between them was not very conspicuous, in general agreement with Wood's early result.

To make a more searching test for polarisation it is usual to employ a Savart polariscope, *i.e.* a pair of plane quartz plates cut 45° from the axis and crossed. The fringes observed with this depend upon obliquity. Such an arrangement was not at hand, and I used a slightly wedge-shaped quartz plate, placed immediately in front of the window of the vessel, and therefore approximately in focus along with the primary beam as seen trans-

^{*} Kerchbaum, 'Electrician,' vol. 72, p. 1074 (1914).

^{† &#}x27;Roy. Soc. Proc.,' A, vol. 98, p. 284 (1920).

versely. The principal directions of vibration in the quartz wedge were at 45° to the direction of the primary beam from the arc. Thus, as we go along the beam, we photograph it transversely through thicknesses of quartz giving first an odd and then an even number of half-waves' retardation; and if there is any polarisation of the scattered light we ought to get dark and bright bands alternating in the photograph of the beam. This was found to be the case, and the bands could be very distinctly photographed right up to the place where the beam entered the vapour. It is clear, therefore, that the light scattered by the resonant vapour is, after all, slightly polarised. This, however, does not go far to bridge over the contrast with the usual cases of scattered white light, which is almost completely polarised.

§ 3. Quantitative Tests. Filtration of Radiation by Mercury Vapour.

To determine the amount of polarisation, I used a method which relies on the constancy of the mercury vapour lamp. It consists in first taking a photograph through the battery of double image prisms. The image in which the vibrations are vertical is the strongest. We now shift the plate so as to bring an adjacent part of it into use, and take another photograph with the lens stopped down, so that with the same exposure the more intense image has the same intensity that the less intense one had before. The diaphragm must be charged and successive photographs taken until this result is attained, as indicated by the photoelectric cell and galvanometer.* The ratio of intensities in the two images is then given by the inverse ratio of lens The method assumes that the double image prisms do not favour one A selective absorption for ultra-violet light, image more than the other. analogous to that shown by tourmaline for visual light, would violate this But it is known that quartz does not show any appreciable effect condition. of this kind for the wave-length in question.†

As already remarked, the quality of the radiation will vary as the beam traverses the column of mercury vapour. The kind of radiation which is most copiously scattered belongs, as Wood has shown, to a very narrow spectral range, and is rapidly removed from the primary beam. Further along, the scattering is much diminished in intensity.

By changing the thickness of mercury vapour traversed, we may, to some extent, examine how the polarisation of the scattered light varies as the resonance frequency is departed from. It is probably a matter of indifference whether the primary or the scattered beam traverses the absorbing column. In my experiments the absorption was chiefly exerted on the primary beam.

^{* &#}x27;Roy. Soc. Proc.,' A, vol. 97, p. 440 (1920).

⁺ With calcite prisms it is appreciable, and gave much trouble until detected.

It is impracticable to allow the primary beam to pass very close to the observing window; if it did so, there would certainly be false light from the latter, so that a short intervening column of mercury vapour cannot be avoided. One of the vessels used was arranged so that the entrance window for the primary beam and the observation window at right angles to it came together at an edge where they were made tight with a little cement. The primary beam was limited by a slit parallel to this edge, and the scattering could be examined immediately it entered the vapour, with only about 4 mm. thickness of mercury vapour for the scattered radiation to traverse.

In this case the weaker component polarisation was measured as 90 per cent. of the intensity of the stronger one.

Another determination was made, using a vessel in which 20 cm. of mercury vapour were traversed by the primary beam, and 7.5 cm. by the scattered beam before coming to the window. In this case the mean of several fairly accordant determinations gave 60 per cent. intensity ratio as compared with the 90 per cent. of the previous case.

The exposure found desirable was sixty times that used before, which will serve to give a rough idea of how greatly the intensity of scattered radiation is reduced by filtering the beam through 27 cm. of mercury vapour. It will be noticed that the mercury vapour used was in vacuo. Mercury vapour in presence of air gives a broader absorption band. It was not used in these experiments.

To get some idea of the spectral range which is approximately cut out by 27.5 cm. of mercury vapour, the structure of the line 2536 from the lamp was examined by a quartz Lummer plate. The fringes were projected by a quartz-fluorite achromat on to the slit of a small quartz spectrograph, in order to separate this line from the others. It appeared that the effect of interposing a column 27.5 cm. long of mercury vapour at room temperature was to cut out the most intense portion of the line having a breadth of 1/100 of an Ångstrom, which was about 1/5 of the entire breadth of the line. The structure of the line appeared to be unsymmetrical. The photographs were definite enough, but more experience than I can claim would be required to interpret them with full confidence.

§ 4. White Light Scattered by Dense Mercury Vapour.

It seemed desirable to make certain that mercury vapour in scattering white light would behave like air and the ordinary gases. For this purpose it was necessary to use dense vapour, since the scattering is so much less powerful than in the case of ultra-violet resonance. The vapour of mercury boiling or nearly boiling at atmospheric pressure was used. The vessel was one of

cross shape, made of steel tube acetylene welded, the same, in fact, as that used for my experiments on scattering by carbon dioxide at high pressure.*

The light from a carbon arc was made parallel by a lens and entered by a mica window, and the scattered light was observed through a window of silica glass, ground and polished. These windows had the advantage of not cracking, which glass windows were very apt to do under the conditions used. The windows were merely held against the ends of the steel tubes, without packing or cement. The whole was placed in an electrically heated oven, with holes corresponding to the windows, and special heaters were arranged to make sure that the windows were hotter than the rest of the vessel, so that no mercury could condense upon them. The vessel was open to the air through an exit tube which served as a reflux condenser.

A little mercury was poured in over-night, and the heating current turned on. By morning, all the liquid mercury had apparently gone, but on turning on the arc it was observed that the track of the beam was of sky-blue colour† and much more intense than in dust-free air. At the same time the polarisation was approximately complete. So far as visual observation could show, all the light was concentrated in one of the images formed by a double image prism.

For whatever reason, dust was not observable in this experiment. The high temperature seems in some way to clear it off.

On adding more liquid mercury, ebullition began, and the disturbance caused dust to rise with the vapour. The individual dust particles could be seen, comparatively yellow in colour, showing by contrast against the blue background formed by the gaseous atmosphere of mercury. The yellow particles showed in both images, but the blue background only in one, as before. Reflex condensation could be seen in the glass exit tube all the time.

The heating current was switched off, and the dust cloud slowly diminished, leaving a blue beam as before. It was confirmed by photography that the light was polarised with approximate completeness. The experiment was not pushed to the point of examining the small defect of polarisation if any. It was considered to establish definitely that mercury vapour behaves to a first approximation like ordinary gases in scattering polarised white light at right angles to the incident beam.

§ 5. Possible Explanation by Rotation of Luminous Centres.

Very little is known about the rotation of molecules, and according to the classical mechanics the monatomic mercury molecule, which has a ratio of

^{* &#}x27;Roy. Soc. Proc.,' A, vol. 95, p. 173 (1918).

⁺ At least to my eyes.

specific heats 1.66, should have no rotational energy. No one, however, would be disposed to press such a conclusion without reserve at the present time, and it may be noticed that a rotation of the emitting centre about the line of vision would destroy the polarisation of the emitted light, if we suppose the emission to be maintained during a rotation of 90° or more, and the direction of vibration to be fixed within the molecule. In the absence of any notion of the angular velocity, we cannot say what duration would be required, but it seems conceivable that in the case of exact resonance the duration might be long enough for this cause to be effective. It was attempted to bring it into evidence by causing the mercury vapour to move as rapidly as possible across the direction of the primary beam, but without effect. There was no tendency for the source of secondary emission as a whole to move downstream.

In these experiments the vessel was a vertical brass tube about 2 cm. square in section, with entrance and observation windows in adjacent sides, and at the same level. These windows were of silica, cemented on with sealing wax, which was found to stand the moderate temperatures used in distillation. Above the level of the windows was an annular gallery containing mercury, the walls of the tube forming the inner railing of the gallery. Below, the closed end of the tube contained granular charcoal, and was immersed in liquid air. This formed the condenser. The tube was thoroughly exhausted with an air pump, and the charcoal kept the exhaustion good, in spite of any tendency of the blackened walls to give off gas. These various conditions were designed to give as free a distillation as possible of rare mercury vapour down the tube.

Photographs were taken (1) without cooling the charcoal (no distillation); (2) charcoal cooled, mercury at room temperature; (3) charcoal cooled, mercury as hot as the hand could bear.

In all these cases the beam was photographed stretching straight across the vessel, and sometimes when the exposure was long a diffuse luminosity surrounded it, due, no doubt, to tertiary radiation. But in no case was any dissymmetry observed, such as would be produced if a luminous source moved downstream an appreciable distance during emission. It may be assumed that the mercury vapour was moving with molecular velocity, or, at least, with a velocity of that order.

Experiments on somewhat similar lines were made by Phillips,* and he obtained a visual green glow and some ultra-violet radiation of $\lambda 2536$ with it. This could be made to go a long distance. The effect, however, appears to be a secondary one, since it is only a small part of the total

^{* &#}x27;Roy. Soc. Proc.,' A, vol. 89, p. 39 (1913).

radiation λ 2536 which can have its origin displaced. To bring out Phillips' effect requires a more vigorous distillation than could be set up in the metal vessel above-mentioned with flat windows and sealing-wax joints. The advantage of this construction is in avoidance of stray light. Phillips used a silica tube strongly heated, so as to give abundant distillation. Such a tube will stand the heat, but is much less favourable in respect of stray light.

It looks as if the centres capable of being excited to durable luminosity were few, and that much mercury must be passed in order to obtain a sufficient supply of them. But there is still a great deal to be done in elucidating the effect, and I do not wish the above suggestion to be taken as more than tentative.

§ 6. Conclusion.

Finally, it is to be remarked that the resonance radiation of mercury is completely lost if the vessel containing the vapour is not exhausted of air. There is no reason to suspect that anything analogous to this occurs when a mixture of ordinary gasses is scattered by white light, and certainly existing theories of the latter phenomenon do not contemplate anything of the kind. As long as this peculiarity remains unexplained, some reserve is necessary in treating resonance radiation as a case of ordinary scattering.

The chief results of the present investigation are :-

- (1) White light scattered at right angles by dense mercury vapour is, to a first approximation, completely polarised.
- (2) Ultra-violet radiation of the mercury spectrum line λ 2536, when examined immediately it enters mercury vapour in an exhausted vessel at room temperature, gives a scattered radiation which is slightly, though definitely, polarised.
- (3) This polarisation has been observed to increase as the beam is filtered by penetration of a considerable depth of vapour. After penetration of 27.5 cm. of vapour the weaker polarised image had 60 per cent. only of the intensity of the stronger one, instead of 90 per cent. as at first. The radiation removed by the filtration appears to lie within a spectral range of about 1/100 Ångstrom.